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(54) Dispersed aqueous suspensions

(57) A method of producing a dispersed aqueous suspension of an inorganic particulate material which includes the steps of (a) preparing an aqueous suspension of calcium carbonate particles having a particle size distribution such that at least 35% by weight have an esd less than 2μm, the solids concentration of the suspension being no more than 40% by dry weight; (b) concentrating the suspension by dewatering to increase the solids content to at least 60% by dry weight; and (c) adding a dispersing agent to the concentrated suspension to disperse the calcium carbonate particles and characterised in that the suspension produced by step (c) is pumpable and flowable, the dispersing agent comprising a water soluble copolymer of acrylic acid and maleic acid or a salt thereof having a molar ratio of acrylic acid units to maleic acid units of from 0.5:1 to 10:1 and a mass average molecular mass of from 1,000 to 100,000.

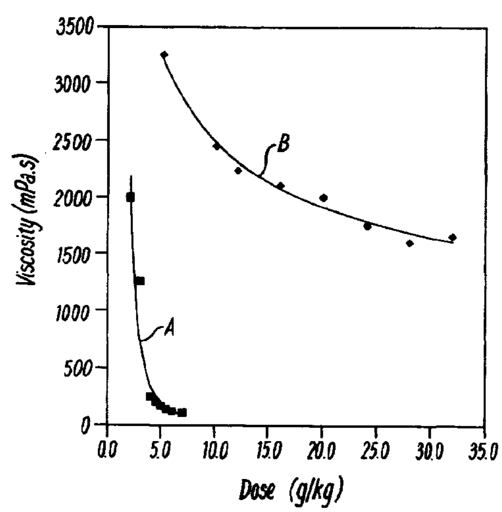

FIG. 1

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Description

The present invention relates to dispersed aqueous suspensions. In particular, it relates to dispersed aqueous suspensions of inorganic particulate material and to the production of such suspensions.

Aqueous suspensions of inorganic particulate material, eg. comprising calcium carbonate or kaolin are used widely in a number of applications, eg. to produce pigment or filler containing compositions which may be used in paper manufacture or paper coating or in the production of filled compositions for paints, plastics and the like. Where such suspensions are required in a high solids form it is necessary to disperse the particulate material using a dispersing agent. In many cases, the dispersing agent limits one or more of the properties of the product, eg. its viscosity, its solids concentration or its particle size distribution. The amount of dispersing agent used may need to be limited by a user on cost grounds.

Sodium polyacrylate is the most widely used dispersing agent for inorganic particulate materials such as calcium carbonate. However, in some situations, use of sodium polyacrylate is not ideal. For instance in certain applications requiring high solids concentrations as described hereinafter required dose rates of sodium polyacrylate are too high and therefore too costly, the product viscosities obtained upon dispersion and after a period of time, eg. at least 24 hours, are too high and the suspension solids level has to be reduced to an unacceptably low level to compensate.

According to the present invention in a first aspect there is provided a method of producing a dispersed aqueous suspension of an inorganic particulate material which includes the steps of (a) preparing an aqueous suspension of calcium carbonate particles having a particle size distribution such that at least 35% by weight have an esd less than 2μm, the solids concentration of the suspension being no more than 40% by dry weight; (b) concentrating the suspension by dewatering to increase the solids content to at least 60% by dry weight; and (c) adding a dispersing agent to the concentrated suspension to disperse the particles of the inorganic particulate material and characterised in that the suspension produced by step (c) is pumpable and flowable, the dispersing agent comprising a water soluble copolymer of acrylic acid and maleic acid or a salt thereof having a molar ratio of acrylic acid units to maleic acid units of from 0.5:1 to 10:1 and a mass average molecular mass of from 1,000 to 100,000, preferably from 1,000 to 10,000.

The inorganic particulate material may comprise calcium carbonate and/or kaolin.

By 'esd' is meant the particle equivalent spherical diameter as measured by the well known technique of sedimentation.

Preferably, the viscosity of the suspension is between 100mPa.s and 600mPa.s especially between 200mPa.s and 500mPa.s on formation.

In this specification, all suspension viscositites refer to measurement at ambient temperature (22°C) using a Brookfield Viscometer set to operate at a spindle speed of 100 rpm. We employed the following procedure in the measurement of viscosities of suspension samples. The suspension was thoroughly mixed using a homogeniser. Immediately after homogenisation the suspension was transferred to the viscometer. The viscometer spindle was immersed in the suspension. The viscometer spindle was activated 30 seconds after cessation of homogenisation and the viscosity was recorded a further 15 sec later.

The method according to the first aspect may be one wherein the viscosity of the suspension produced in step(c) if alternatively dispersed with a polyacrylic acid having the same molecular mass and the same degree of neutralisation as the said copolymer of acrylic acid and maleic acid instead of the said copolymer has a viscosity which is greater than 1,000mPa.s.

The said dispersing agent may comprise a partially or wholly neutralised salt of the said copolymer. Such a salt may comprise for example an alkali metal salt, eg. a sodium salt, or an ammonium salt of the copolymer of acrylic and maleic acids. Desirably the molecular mass is in the range 1,000 to 30,000 especially 1,500 to 10,000, eg. 2,000 to 8,000 on a mass average basis.

Steps (a) and (b) may be carried out to produce or process the said calcium carbonate particles in a known manner. Examples of processes using such steps and beneficially embodying the invention are as follows.

Where the said inorganic particulate material comprise calcium carbonate and/or kaolin the particles of the material may be particles which have been ground, eg. using in a known grinding procedure, an attrition grinding medium such as silica, alumina or zirconia, in an aqueous suspension having a low solids concentration, eg. less than 35% by weight. Thus, the product of step (a) in the method according to the present invention may be the product of such attrition grinding.

Step (b) may be carried out to concentrate the suspension to facilitate storage and transport of the suspension product or to use the same in a high solids application, eg. as a pigment, filler or extender composition for use in paper making, paper coating or in plastics or paints composition.

In processes of this kind it is conventional to avoid use of a dispersing agent in the dewatering step because concentration is carried out with the particulate solids in a flocculated state. Thus, after dewatering the concentrated inorganic particulate material obtained, eg. a high solids filter cake, may comprise a flocculated body whose constituent particles require redispersion. As exemplified hereinafter, the redispersion may beneficially be carried out using the method according to the first aspect of the invention.

The inorganic particulate material may alternatively comprise precipitated calcium carbonate (pcc) pro-

duced in a known way by a chemical precipitation reaction low solids aqueous suspension, eg. having a solids concentration less than 25% by weight. The particles may be predominantly of a preferred crystal form; eg. scalenohedral, rhombohedral or aragonite, obtained by applying known reaction conditions which favour the growth of crystals of the preferred form. The particles may be the product of reaction of gaseous carbon dioxide with calcium hydroxide in a slaked lime suspension in a manner well known to those skilled in the art. Dewatering of the dilute precipitate-containing suspension produces a concentrated solid, eg. filter cake, similar to the concentrated solid material produced by grinding as described hereinbefore. The concentrated solid may beneficially be redispersed in accordance with the present invention as exemplified hereinafter. Such a dispersed, concentrated suspension may be used in compositions for the applications described hereinbefore.

The particle size distribution (PSD) of the product obtained may be selectively steep, eg. the percentage of particles less than a given value plotted against the logarithm of the particle size may show an inverted 's'-shaped region as will be familiar to those skilled in the art, eg. as described in US 5,292,365. For example, the PSD steepness factor which may be defined as particle diameter in μm at 50% by weight ÷ particle diameter in μm at 20% by weight as obtained from the PSD curve, may be less than 2.0, eg. less than 1.7.

Although it is desirable to achieve by use of the method according to the first aspect of the present invention a pumpable, flowable slurry, eg. having a dry solids content of at least 60% by weight, it is also desirable for the resultant slurry not to be excessively fluid. In storage and transport of such excessively fluid slurries it is necessary to include a suspension aid, eg. an alginate, in the slurry to prevent unwanted sedimentation. The viscosity of the slurry product therefore is desirably in the range of from 100mPa.s to 500mPa.s, especially 200mPa.s to 400mPa.s, to avoid use of the suspension aid which adds to the cost of the slurry. The slurry may be obtained in the desired viscosity range either by (i) blending an acrylic acid/maleic acid copolymer individually giving a very fluid slurry, eg. having a viscosity less than 100mPa.s, with an alternative dispersing agent, eg. a water soluble polyacrylic acid or a salt thereof, individually giving a higher viscosity, eg. greater than 1000mPa.s under similar conditions or (ii) using an acrylic acid/maleic acid copolymer or salt thereof having an acrylic:maleic molar ratio selected to give the required viscosity. For example, where a sodium salt of a copolymer of acrylic and maleic acids having a molar acrylic to maleic ratio of 2:1 gives a slurry viscosity of less than 100mPa.s it may be suitable to use as dispersing agent a sodium salt of an acrylic acid/maleic acid copolymer having a molar acrylic to maleic ratio of from 3:1 to 9:1, especially 5:1 to 7:1, to give the required slurry viscosity of 100mPa.s to 500mPa.s, especially 200mPa.s to 400mPa.s.

In the method according to the first aspect of the present invention the dewatering step may be carried out using a known procedure, eg. using filtration, eg. with a filter press of the tubular kind, evaporation, eg. forced evaporation under reduced pressure or centrifugation.

According to the present invention in a second aspect there is provided a dispersed aqueous suspension which is the product of the method according to the first aspect.

The suspension according to the second aspect may have a viscosity in the range 100mPa.s to 500mPa.s and desirably remains in that range after at least 24 hours after formation. The copolymer dispersing agent may be present in the suspension in an amount of from 0.1% to 2% by weight based upon the dry weight of the solids present in the suspension. The suspension may have a solids content of greater than 60% by dry weight, eg. greater than 70% by weight.

Copolymers of acrylic and maleic acids are known in the prior art. However, the benefits unexpectedly obtained by selection of such copolymers from the many known anionic water soluble dispersing agents for the particular task of dispersing inorganic particulate materials in a concentrated aqueous suspension following preparation and/or processing at low solids and subsequent concentration without dispersing agent is not known or suggested in the prior art.

Embodiments of the present invention will now be described by way of example with reference to the following Examples and the accompanying drawings, in which:

Figures 1 to 4 are graphs of viscosity versus active dispersing agent dose for aqueous mineral suspensions treated in accordance respectively with an embodiment of the present invention and using a prior art procedure.

Curve A in each of Figures 1 to 4 represents use of a maleic/acrylic copolymer in accordance with an embodiment of the invention and Curve B in each case represents use of sodium polyacrylate in accordance with the prior art.

Example 1:

Preparation of Steep PSD Ground Calcium Carbonate

Calcium carbonate was produced by grinding marble chips in an aqueous suspension at low solids (less than 25% by weight) using a grinding method as described in EP 614948.

No dispersing agent was present.

The particulate product had a particle size distribution such that at least 90% by weight of the particles had an esd of less than 2μm. The product was concentrated to a solids concentration of 70% by weight using a filter press to form a flocculated, high solids filter cake. This was redispersed in water using two alternative dispers-

ing agents A and B in varying doses. For each dispersed slurry so formed the values of T_0, T_1, and T_{24} viscosity were measured in the manner described hereinbefore, where T_0, T_1 and T_{24} viscosity is the viscosity of the suspension (a) immediately after preparation, (b) after standing for a period of 1 hour and (c) after standing for a period of 24 hours.

In these experiments dispersing agent A was the sodium salt of an acrylic/maleic acid copolymer having a 2:1 molar acrylic/maleic ratio and average molecular mass of 4000. Dispersing agent B was sodium polyacrylate (Dispex N40 supplied by Allied Colloids Ltd, Mw≅ 4,000).

Figure 1 shows a plot of initial T_0 viscosity versus active dispersing agent dose for the two dispersing agents. Curve A shows the plot for dispersing agent A and curve B shows the plot for dispersing agent B.

Figure 1 shows that:

(i) for sodium polyacrylate (curve B) the initial viscosity (T_0) gradually dropped from 3250 mPa.s to 1600 mPa.s after a total addition of 28.0 g per kg of calcite;
(ii) for the acrylic/maleic copolymer (curve A) additions of 4.0g per kg of calcite resulted in a reduction in T_0 viscosity from above 3000 mPa.s to 250 mPa.s. Further copolymer addition gave a minimum T_0 viscosity of 100 mPa.s (7.00g per kg of calcite) ;
(iii) only small increases in viscosity with time were seen with both dispersing agents. However, the T_1 and T_{24} viscosities observed with the acrylic/maleic copolymer were, of course, much lower than those with sodium polyacrylate.

The sharp fall in slurry viscosity at low levels on acrylic/maleic copolymer addition to very low viscosity values and the small variance of this low viscosity throughout the remainder of the copolymer dose range illustrates that the acrylic/maleic copolymer has much greater efficacy for stabilising pre-ground calcite dispersions than sodium polyacrylate.

Example 2

Pcc which was predominantly scalenohedral in crystal form was produced by bubbling carbon dioxide gas through a 2m slaked lime suspension in a known manner. The solids concentration of the suspension was 20 weight %. The suspension was concentrated as in Example 1 to form a filter cake which was redispersed in water containing separately dispersing agents A and B as employed in Example 1. The solids concentrations of the suspensions formed, based on the dry weight of the pcc present, was in three separate experiments respectively 36.6%, 64.5% and 69%. The T_0 viscosity as a function of dispersing agent dose rate was measured for dispersing agents A and B at these three solids concentrations. The results obtained for the three suspension concentrations are plotted graphically in Figures 2 to 4 respectively where, in each case, curve A represents use of dispersing agent A and curve B represents use of dispersing agent B.

The results show the following:

(i) at a solids concentration of 36.6% (Figure 2) dispersing agent A (curve A) shows no advantage over dispersing agent B (curve B);
(ii) a solids concentration of 64% (Figure 3) suspensions using dispersing agent B (curve B) show unacceptably high viscosities whereas suspensions using dispersing agent A (curve A) show acceptable viscosities for active dose rates above about 1.10 weight %;
(iii) at a solids concentration of 69% weight acceptable viscosities are still obtained with dispersing agent A (curve A). Curve B does not appear in Figure 4 because the measured viscosities are so high.

Example 3

Ground calcium carbonate was produced having a particle size distribution such that about 60% had an esd less than 2µm. The grinding was carried out by sand milling at a solids concentration of about 30 weight %. The suspension was dewatered using a rotary vacuum filter. The suspension was dispersed with a sodium polyacrylate dispersing agent as employed in Example 1. The viscosity was unacceptably high. The suspension was too viscous to process and to pump and was likely to set in transit.

The suspension obtained after dewatering was alternatively dispersed using copolymer dispersing agent A as used in Example 1. A minimum suspension viscosity of 60 mPa.s was obtained at an active dispersing agent dose rate of 0.4 weight %. Such a suspension is very fluid as discussed hereinbefore. The viscosity was raised to a more suitable value of about 300 mPa.s by addition of a viscosity raising agent, eg. an alginate or an alternative dispersing agent. A blend of dispersing agent A together with an alternative dispersing agent C which was a sodium salt of an acrylic/maleic copolymer having an acrylic:maleic molar ratio of 10:1, (mass average molecular mass = 4,000) the blend containing agents A and C in the weight ratio 1:2 (A:C), was found to give a suitable viscosity at an active dispersing agent dose of 0.4% by weight.

The suspension obtained after dewatering was alternatively dispersed using only a further dispersing agent D which was the sodium salt of an acrylic/maleic copolymer having an acrylic to maleic ratio of 6:1 and a mass average molecular mass of 4,000 at an active dose amount of 0.4% by weight.

The suspensions obtained using dispersing agents A and C and separately D both showed the required viscosity of about 300 mPa.s.

Claims

1. A method of producing a dispersed aqueous suspension of an inorganic particulate material which includes the steps of (a) preparing an aqueous suspension of calcium carbonate particles having a particle size distribution such that at least 35% by weight have an esd less than 2µm, the solids concentration of the suspension being no more than 40% by dry weight; (b) concentrating the suspension by dewatering to increase the solids content to at least 60% by dry weight; and (c) adding a dispersing agent to the concentrated suspension to disperse the calcium carbonate particles and characterised in that the suspension produced by step (c) is pumpable and flowable, the dispersing agent comprising a water soluble copolymer of acrylic acid and maleic acid or a salt thereof having a molar ratio of acrylic acid units to maleic acid units of from 0.5:1 to 10:1 and a mass average molecular mass of from 1,000 to 100,000.

2. A method as claimed in claim 1 and wherein the viscosity of the suspension is not greater than 600mPa.s on formation.

3. A method as claimed in claim 2 and wherein the viscosity of the suspension is between 200mPa.s and 400mPa.s on formation.

4. A method as claimed in claim 1, claim 2 or claim 3 and wherein the suspension produced in step(c) is such that if alternatively dispersed with a polyacrylic acid having the same molecular mass and the same degree of neutralisation as the said copolymer of acrylic acid and maleic acid instead of the said copolymer has a viscosity which is greater than 1,000mPa.s.

5. A method as claimed in claim 1, claim 2, claim 3 or claim 4 and wherein the inorganic particulate material comprises calcium carbonate and/or kaolin particles which have been ground using an attrition grinding medium in an aqueous suspension having a solids concentration less than 35% by weight.

6. A method as claimed in claim 1, claim 2, claim 3 or claim 4 and wherein the inorganic particulate material which comprises precipitated calcium carbonate (pcc) produced in a low solids aqueous suspension having a solids concentration less than 25% by weight.

7. A method as in claim 6 and wherein the particles are predominantly of a preferred crystal form selected from scalenohedral, rhombohedral and aragonite applying known reaction conditions which favour the growth of such crystals.

8. A method as claimed in any one of the preceding claims and wherein step (c) is carried out using a dispersing agent obtained by blending an acrylic acid/maleic acid copolymer individually giving a fluid slurry having a viscosity less than 100mPa.s, with an alternative dispersing agent, individually giving a higher viscosity greater than 1000mPa.s under similar conditions.

9. A method as claimed in any one of claims 1 to 7 and wherein step (c) is carried out using as dispersing agent an acrylic acid/maleic acid copolymer or salt thereof having an acrylic:maleic molar ratio of from 3:1 to 9:1 to give a required slurry viscosity of 100mPa.s to 500mPa.s, especially 200mPa.s to 400mPa.s.

10. A dispersed aqueous suspension which is the product of the method according to any one of claims 1 to 9.

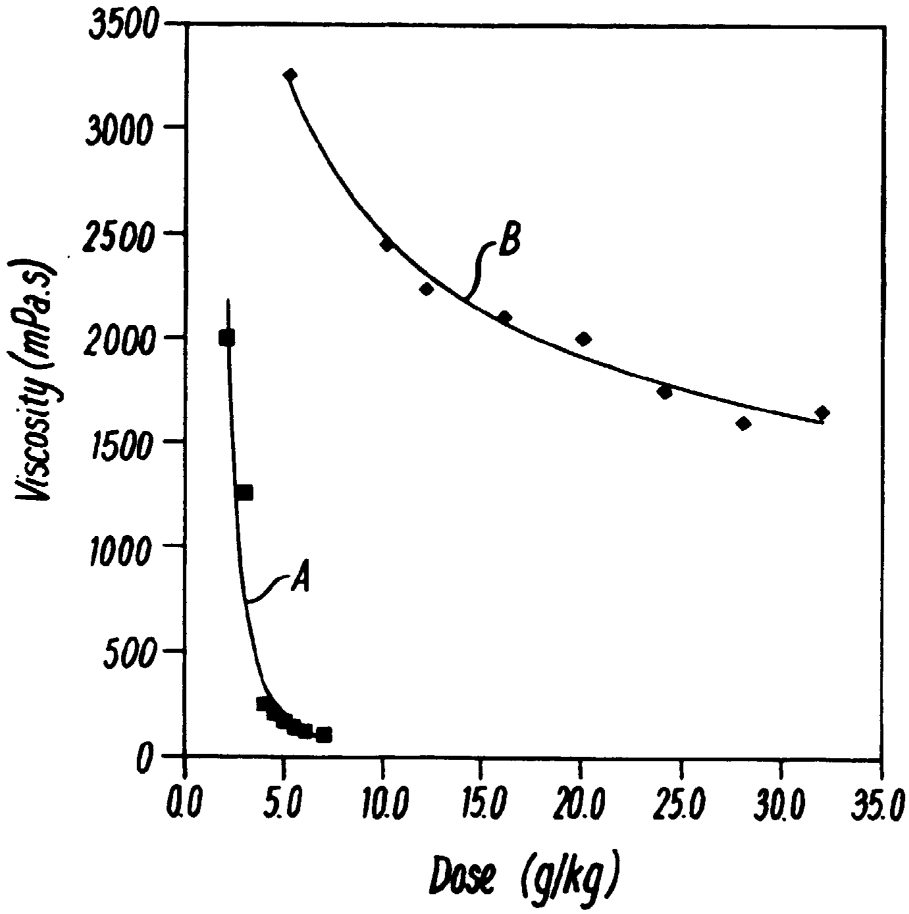
3500
3000
2500
2000
1500
1000
500
0
Viscosity (mPa.s)
B
A
0.0
5.0
10.0
15.0
20.0
25.0
30.0
35.0
Dose (g/kg)

FIG. 1

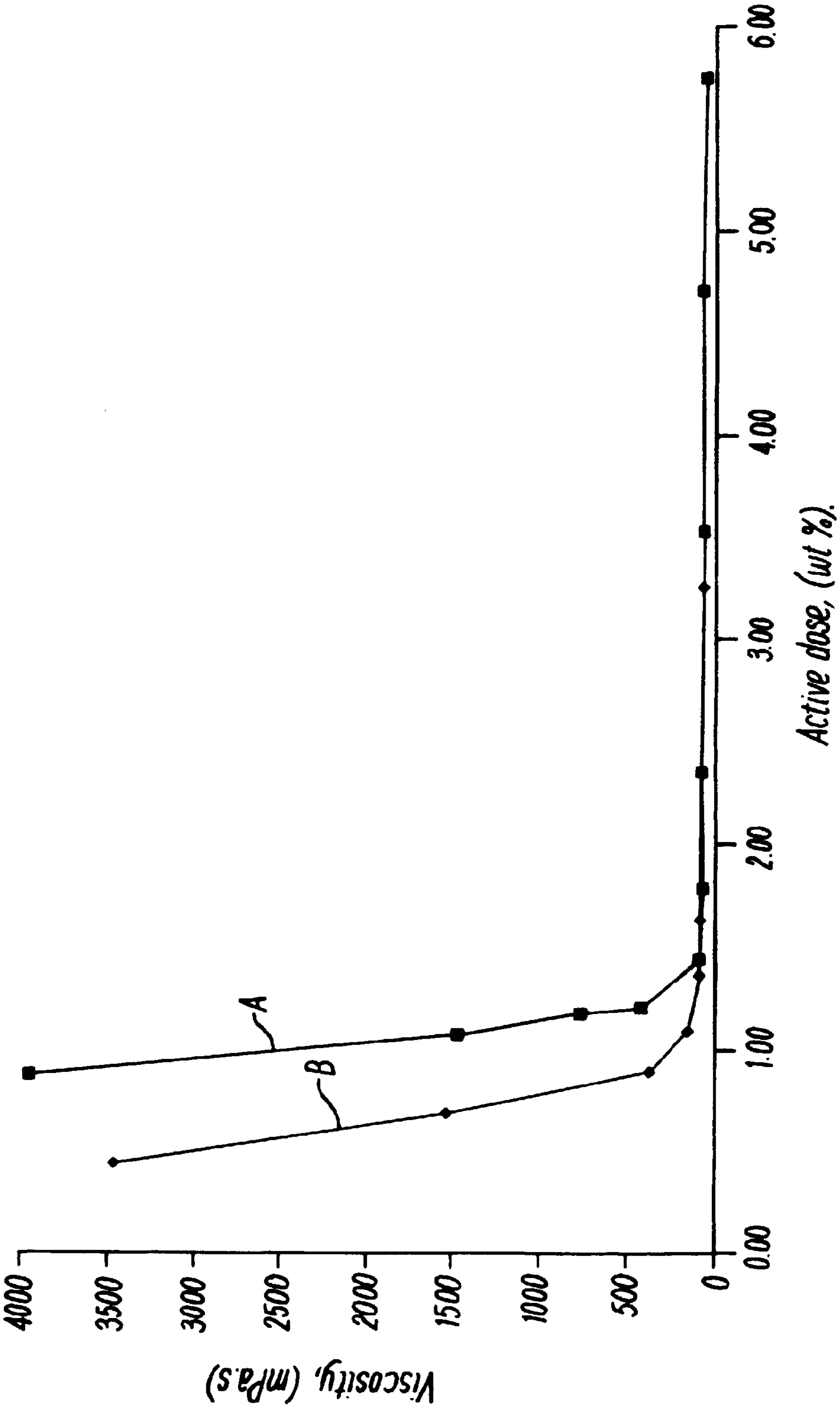
Viscosity, (mPa.s)
4000
3500
3000
2500
2000
1500
1000
500
0
0.00
1.00
2.00
3.00
4.00
5.00
6.00
Active dose, (wt %).
A
B

Fig. 2

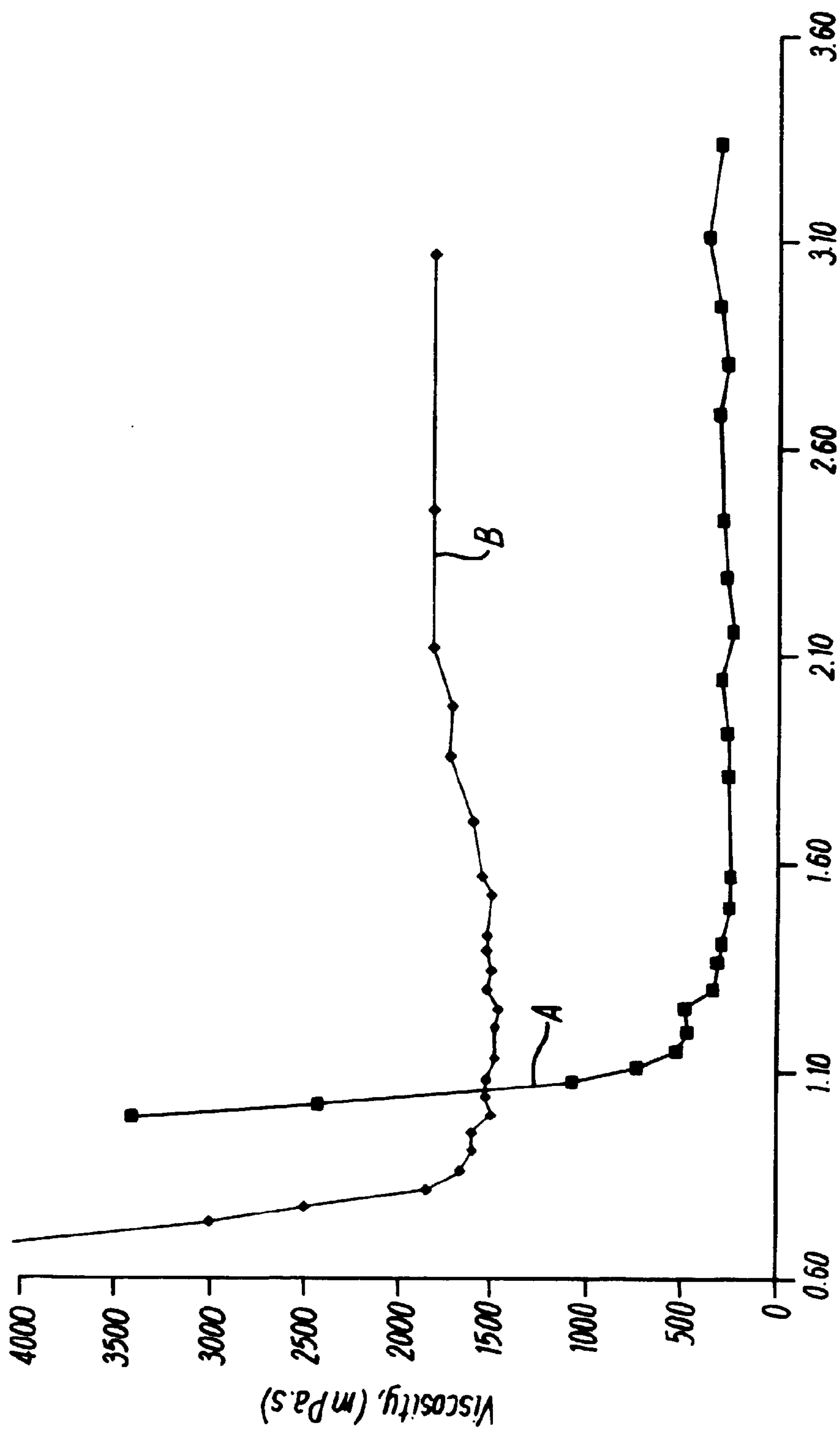
Viscosity, (m Pa.s)
0
500
1000
1500
2000
2500
3000
3500
4000
Active dose, (wt %).
0.60
1.10
1.60
2.10
2.60
3.10
3.60
A
B

Fig. 3

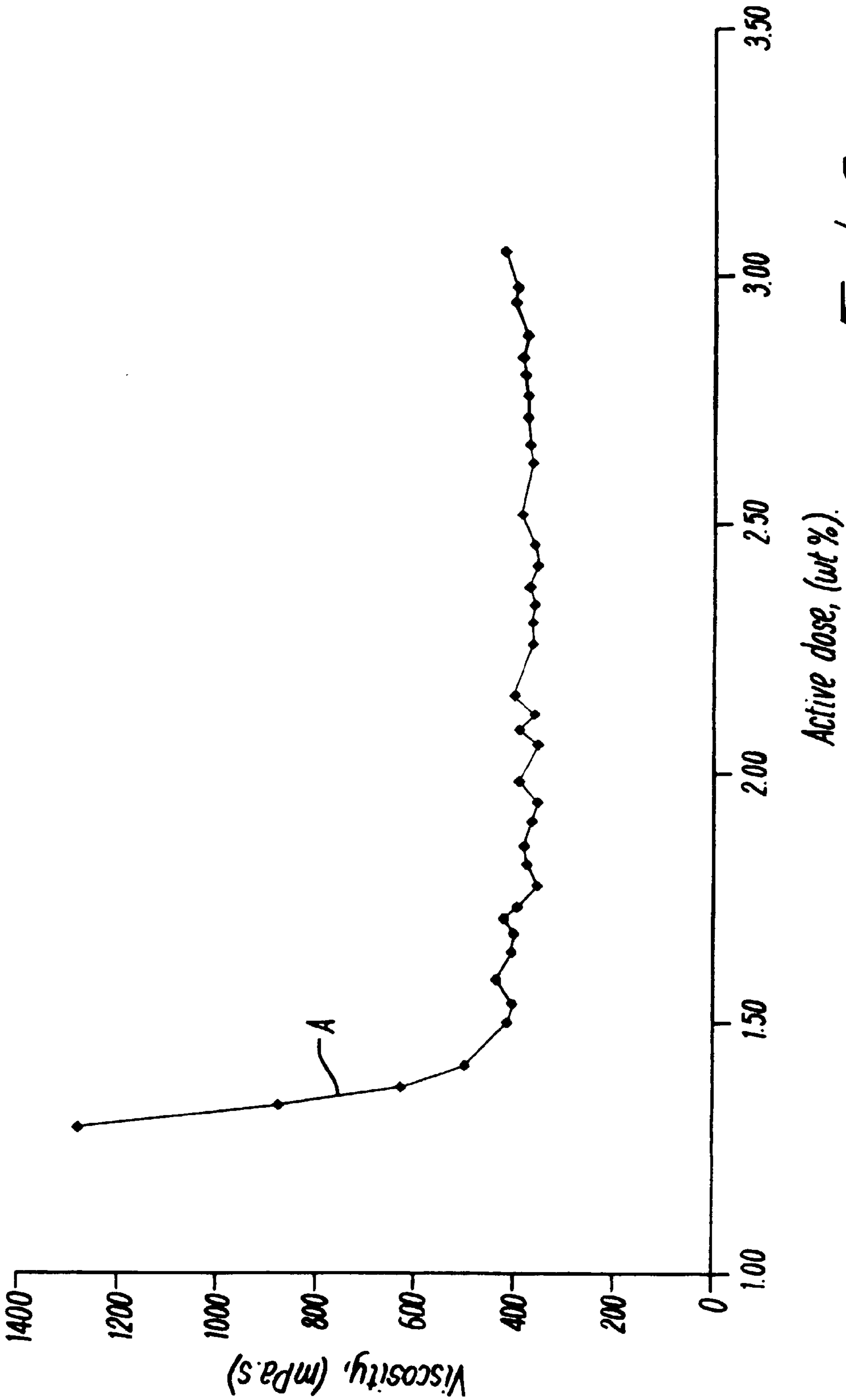
Viscosity, (mPa.s)
0
200
400
600
800
1000
1200
1400
Active dose, (wt %).
1.00
1.50
2.00
2.50
3.00
3.50
A

Fig. 4